Report for 2004MO31B: Use of Excitation/Emission Matrix Fluorescence

There are no reported publications resulting from this project.

Report Follows

An annual report submitted to Missouri Water Resources Research Center/USGS

Use of Excitation/Emission Matrix Fluorescence for Wastewater Sources Identification

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ABSTRACT

Water contamination can come from different sources, including wastewater treatment effluent, landfill leachate, agricultural runoff, and a wide variety of industrial sources. Identifying and differentiating these sources are needed to effectively manage the water pollution issues and enforce the environmental regulation. The objective of this project is to establish a fluorescence excitation/emission matrix database for different types of water and to develop a mathematical procedure/computer model to identify the source of unknown water samples. The research tasks include: (i) collections of substantial numbers of water samples from various known sources, (ii) analysis of water samples for excitation/emission spectra, and (iii) development of a mathematical/ computer model that can be used to identify different sources of water. In this project period, we have made significant progress on tasks (i) and (ii), including procurement, installation, and testing of the a Hitachi F-4500 fluorescence spectrophotometer; analysis of pure water samples and individual chemical dissolved in water; and analysis of 60 Missouri water samples from various lakes and water supplies.

Introduction

Molecular fluorescence spectroscopy is an analytical technique based on emission of fluorescence from a molecule upon excitation by irradiation. It is a rapid and inexpensive way of wastewater identification and quantification, in particular, when excitation/emission matrix spectra (EEMS) in a wide range of wavelength are collected. Compounds containing aromatic rings normally give the most intense molecular fluorescence emission, including benzene, toluene, phenol, quinoline, and many fused ring aromatic compounds. A small number of aliphatic and alicyclic carbonyl compounds with highly conjugated double-bound structures also fluorescence. Since fluorescence spectroscopy is much more sensitive than absorption spectroscopy, it is particularly suitable for trace amounts of contaminant detection.

The objective of this project is to establish a fluorescence EEMS database for different types of water in the state of Missouri and develop a mathematical procedure/computer model to identify the source of unknown water samples. Different types of waters have their own fluorescence features as they contain various fluorescence species. The fluorescence characteristics of river water (Yan et al., 2000), seawater (Coble et al., 1990; Coble, 1996), groundwater (Baker and Genry, 1999; Baker and Lamont-Black, 2001), sewage, and sewage-impacted river water (Reynolds and Ahmad, 1997; Baker, 2001, 2002) have been documented separately. However, by now, there is no database that provides comprehensive fluorescence spectra for various types of water. This research aims to fill the data gap by building a much more comprehensive database critical for the source identification of the unknown wastewater samples.

Experimental Section

1. Instrument Description and Parameters for Data Collection

We have acquired a Hitachi F-4500 fluorescence spectrophotometer for the current study. This is a research grade, easy to use fluorescence spectrophotometer with its FL Solutions® software for rapid data acquisition (2400nm/min-30,000 nm/min).

<u>Instrument Features</u> (Courtesy of Hitachi)

- Three-dimensional contour plots provide maximum spectral information and can be acquired and displayed in less than one minute.

- Phosphorescence is built-in as standard and allows lifetime measurements from 1 ms to address the widest range of samples.

- In addition to fluorescence and phosphorescence measurements, luminescence is included as standard. The high energy throughput and signal-to noise of the system allow measurements of chemiluminescent and bioluminescent compounds.

- The intense 150 watt xenon source provides maximum light energy over the entire 200-900 nm wavelength range of the spectrophotometer. A rhodamine B quantum counter is used to determine the correction factors for true instrument response to assure spectral accuracy.

- Unique horizontal beam geometry of the excitation and emission beams increases sensitivity and requires only 0.6 mL of sample in a standard 10mm cuvette.

- Automatic shutter control protects photo sensitive samples from degradation.

The following parameters, as illustrated in Table 1, were set before using the instrument for measurement of excitation and emission spectra. The excitation wavelength was set from 200 to 400 nm and emission wavelength from 250 to 550 nm on 12000nm/min and 30000nm/min scan speed.

Table 1: Calibration set for scanning

Information about sample/instrument		Calibration set for instrument	
Report Date:	5/19/2005 22:11	EX End WL:	400.0 nm
Sample:	Watkins Mill(#74)	EX Sampling Interval:	2.0 nm
File name:	Missouri Water Samples004.FD3	EM Start WL:	250.0 nm
Run Date:	3/11/2005 9:36	EM End WL:	550.0 nm
Operator:	Owner	EM Sampling Interval:	3.0 nm
Comment:	Collected @ 08/09/04	Scan speed:	12000 nm/min
Instrument Model:	F-4500 FL Spectrophotometer	EX Slit:	5.0 nm
Serial Number:	1606-005	EM Slit:	10.0 nm
ROM Version:	4000 05	PMT Voltage:	700 V
Measurement type:	3-D Scan	Response:	Auto
Data mode:	Fluorescence	Corrected spectra:	On
EX Start WL:	200.0 nm	Shutter control:	On

2. Analysis

To establish a database for water source identification, we need to collect water samples from various known sources and analyze the samples for excitation/emission matrix spectra. Up to now, 60 water samples collected from major lakes and water treatment plants and were analyzed. The Milli-Q deionized water and tap water, as well as solutions of individual chemicals with various functional groups were also scanned for excitation and emission spectra to understand the fluorescence characteristics and pattern and intensities. Fluorescence data were collected in the excitation wavelength from 200 to 400 nm and emission wavelength from 250 to 550 nm with 2 and 3 nm intervals respectively.

1. Tap & D.I Water Samples:

Several deionized water samples and tap water from University of Missouri Campus were scanned for excitation and emission matrix spectra. Following are the 3-D scan of each of them. The former shows no fluorescence and latter has some degree of intensity and fluorescence possible because of natural organic matter.

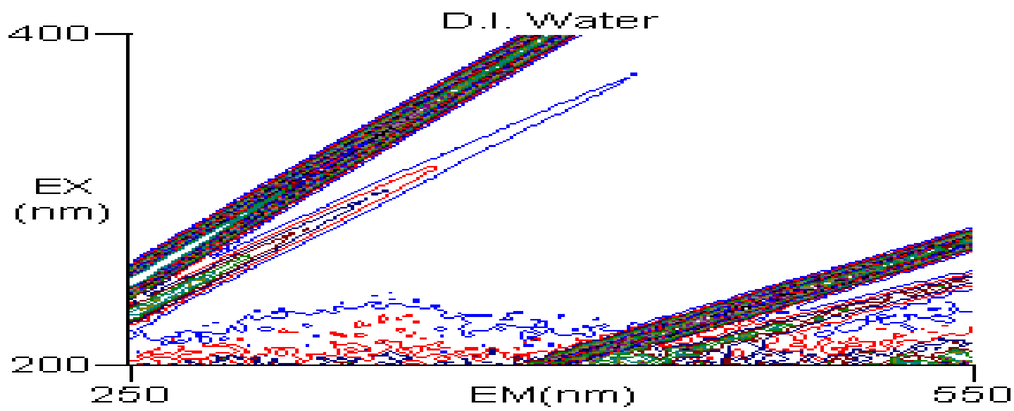

Figure 1

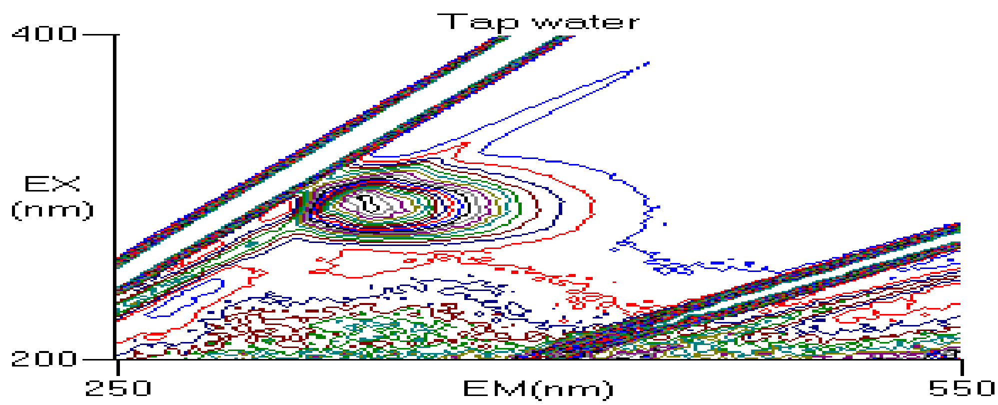

Figure 2

2. Water Samples for Individual Chemicals:

Eighteen chemicals, as listed in Table 2, were scanned at a concentration of 10 ppm for each.

Table 2: List of chemicals and water samples

S.N	Sample Name	Volume (ml)	Conc. (g/l)	Weigh t(g)
1	Benzoic Acid	50	5	0.25
2	Glutamic Acid	50	5	0.25
3	Hydroxybenzoic Acid	50	5	0.25
4	Phenol	50	5	0.25
5	D-Glucose	50	5	0.25
6	4-amino- Pyrine	50	5	0.25
7	1,2 cyclohexylene-dinitrilo tetracetic acid	50	5	0.25
8	Cosmic acid	50	5	0.25
9	5’-5’’-Dibromo-O- creasolesulfonephthalein	50	5	0.25
10	Dimythylamino azobenzene	50	5	0.25
11	1-5 Diphenylcarbazide	50	5	0.25
12	ADA,N(2-Acetamido) Iminodiacetic Acid	50	5	0.25
13	Oxalic Acid	50	5	0.25
14	3-(4-Morpholino)-Propanesulfonic Acid	50	5	0.25
15	2-(4-Morpholino)-Ethanesulfonic Acid	50	5	0.25
16	1,10 Phenanthroline	50	5	0.25
17	Peptone	50	5	0.25
18	2-(2-Thiazolylazo)-p-Cresol	50	5	0.25

The data collected could be visualized by 3-D contour map and Bird’s eye view, as illustrated by Figure 3-6 for hydroxybenzoic acid and D-glucose.

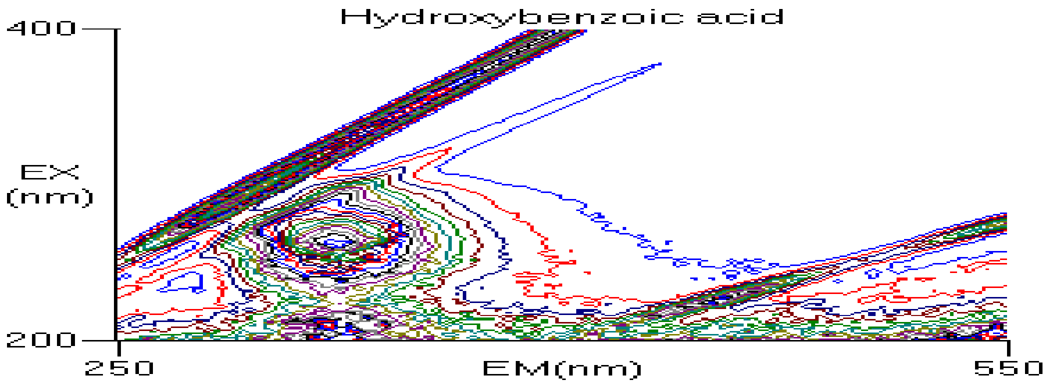

Figure 3: Contour and spectrum of hydroxybenzoic acid

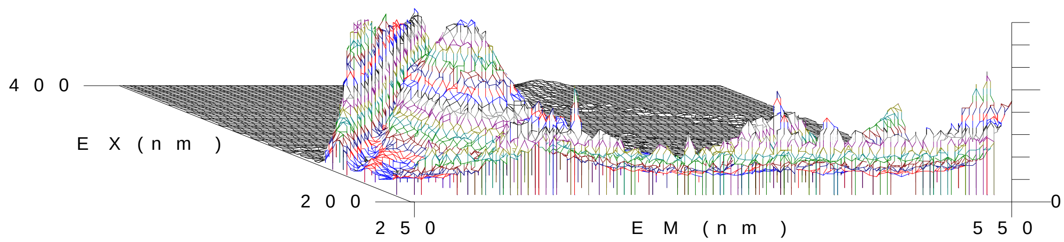

Figure 4: Bird's eye view of Hydroxybenzoic acid

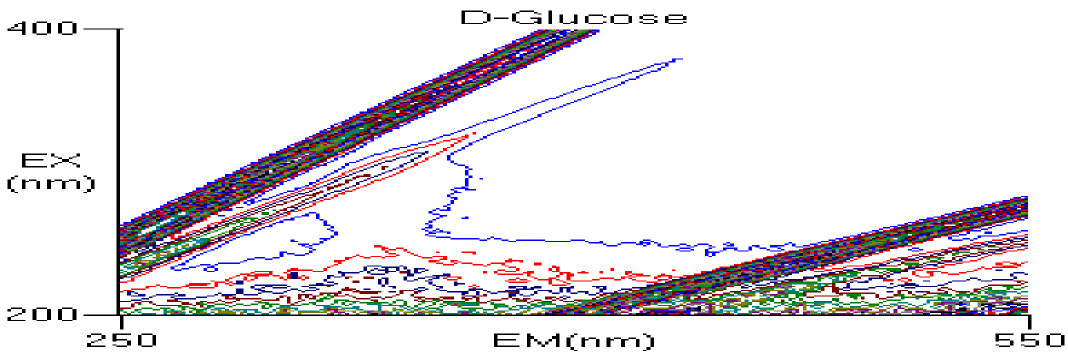

Figure 5 D-Glucose

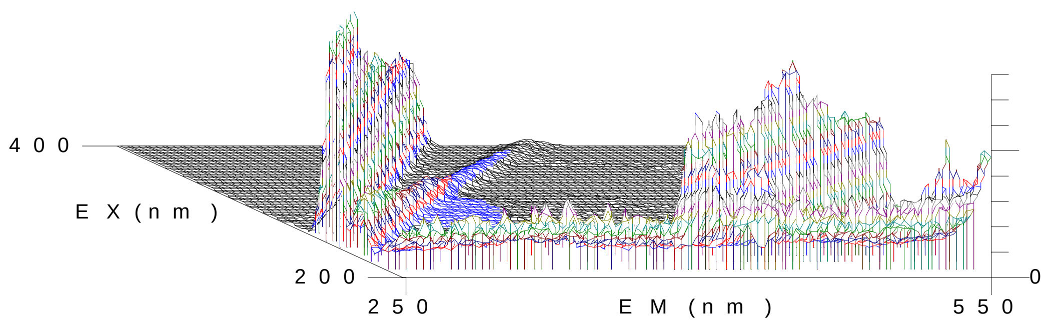

Figure 6: Bird's eye view of D-Glucose

3. Missouri Water Samples

A total of sixty (60) samples were collected through Missouri Water Resources Research Center and scanned for excitation and emission spectra. The samples represent the different rivers, lakes, creeks in the State of Missouri. Table 4 lists the samples scanned for the fluorescence intensity and some EEMS are illustrated in Figures 7-14. .

Table 4: A list of water samples collected for fluorescence analysis

S.N	Collected Date	CE Bottle #	Sample Name	Sample#
1	7/27/2004	7/27-1	Miller Community Lake	35
2	7/27/2004	7/27-3	Clearwater Lake	36
3	7/27/2004	7/27-5	Wapapello Lake	30
4	7/27/2004	7/27-7	Lake Girardeau	28
5	7/27/2004	7/27-9	Boutin Lake	27
6	7/27/2004	7/27-11	Bella Vista Lake	26
7	7/27/2004	7/27-13	Fredericktown City Lake	24
8	7/28/2004	7/28-15	Anne	22
9	7/28/2004	7/28-17	Capri	18
10	7/28/2004	7/28-19	Shane	112
11	7/28/2004	7/28-21	Bismark	186
12	7/28/2004	7/28-23	Council Bluff	39
13	8/3/2004	8/3-1	Monroe Lake	60
14	8/3/2004	8/3-3	Lake Hunnewell	115
15	8/3/2004	8/3-5	Henry Sever	114
16	8/3/2004	8/3-7	LaBelle City	129
17	8/3/2004	8/3-9	Deer Ridge	57
18	8/3/2004	8/3-11	Fox Valley	182
19	8/3/2004	8/3-13	Lancaster City	132
20	8/4/2004	8/4-15	LaPlatta Lake	130
21	8/4/2004	8/4-17	Longbranch	48
22	8/4/2004	8/4-19	Thomas Hill Reservoir	46
23	8/4/2004	8/4-21	Tri-CityCommunity Lake	42
24	8/4/2004	8/4-23	Little Dixie	117
25	8/9/2004	8/9-1	Pape Lake	113
26	8/9/2004	8/9-2	Higginsville	121
27	8/9/2004	8/9-3	Hazel Hill	183
28	8/9/2004	8/9-4	Odessa Lake	64
29	8/9/2004	8/9-5	Watkins Mill	74
30	8/9/2004	8/9-6	Smithville Lake	72
31	8/9/2004	8/9-7	Belcher Branch	187
32	8/10/2004	8/10-8	Raintree	118
33	8/10/2004	8/10-9(not filtrated)	Holden City	157
34	8/10/2004	8/10-10(not filtrated)	North Lake	70
35	8/10/2004	8/10-11(not filtrated)	Butler City	189
36	8/10/2004	8/10-12(not filtrated)	Atkinson	91
37	8/10/2004	8/10-13(not filtrated)	Bushwacker	161
38	8/10/2004	8/10-14(not filtrated)	Stockton	93
39	8/10/2004	8/10-15(not filtrated)	McDaniel	95
40	8/10/2004	8/10-16(not filtrated)	Fellows	96
41	8/11/2004	8/11-17(not filtrated)	Pomme De Terre	92
42	8/11/2004	8/11-18(not filtrated)	Truman	89

43	8/11/2004	8/11-19(not filtrated)	Lake of the Ozarks	149
44	8/11/2004	8/11-20(not filtrated)	Manito	184
45	8/11/2004	8/11-21(not filtrated)	Binder	13
46	8/17/2004	8/17-1	Sterling	119
47	8/17/2004	8/17-2	Nehai Tonkyea	45
48	8/17/2004	8/17-3	Marceline-2	88
49	8/17/2004	8/17-4	Marceline-1	139
50	8/17/2004	8/17-5	Brookfield	87
51	8/17/2004	8/17-6	Hazel Creek	131
52	8/17/2004	8/17-7	Forest	133
53	8/17/2004	8/17-8	Green City	137
54	8/18/2004	8/18-9	Marie	85
55	8/18/2004	8/18-10	Paho	84
56	8/18/2004	8/18-11	New Bethany	83
57	8/18/2004	8/18-12	Harrison Co.	185
58	8/18/2004	8/18-13	Mozingo	181
59	8/18/2004	8/18-14	Nodaway	179
60	8/18/2004	8/18-15	Bilby Ranch	180

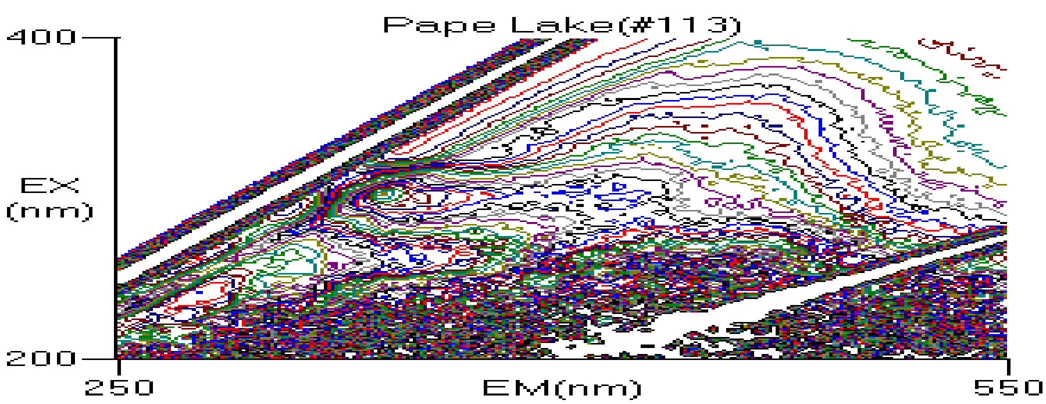

Figure 7

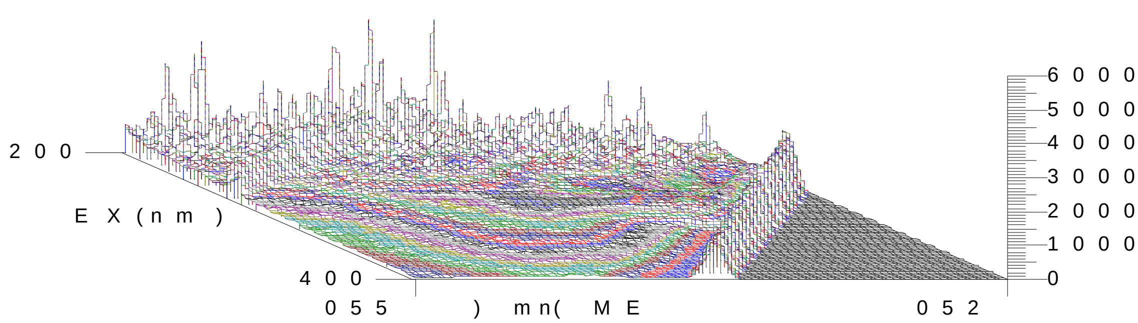

Figure 8

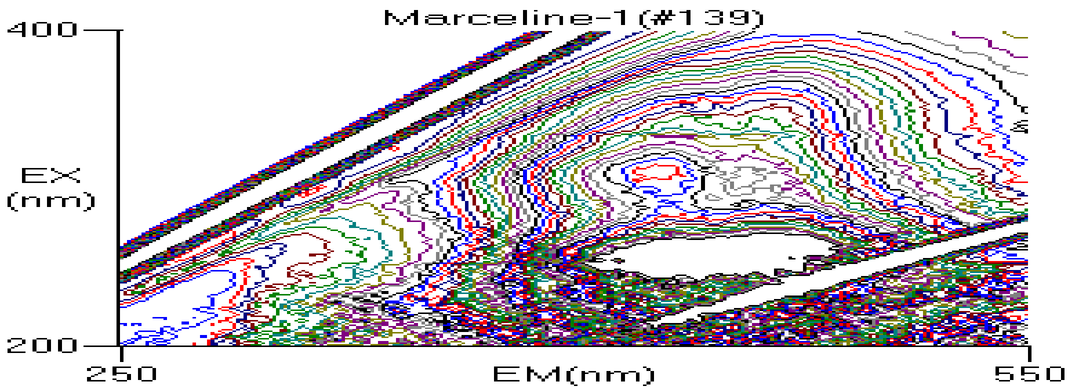

Figure 9

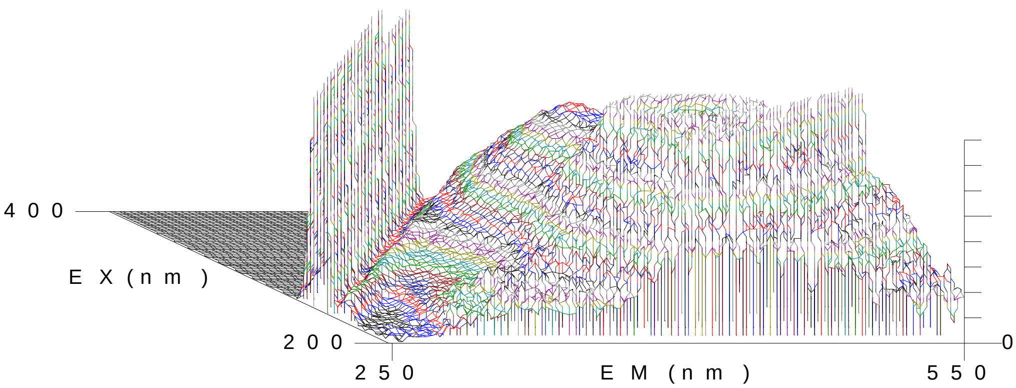

Figure 10

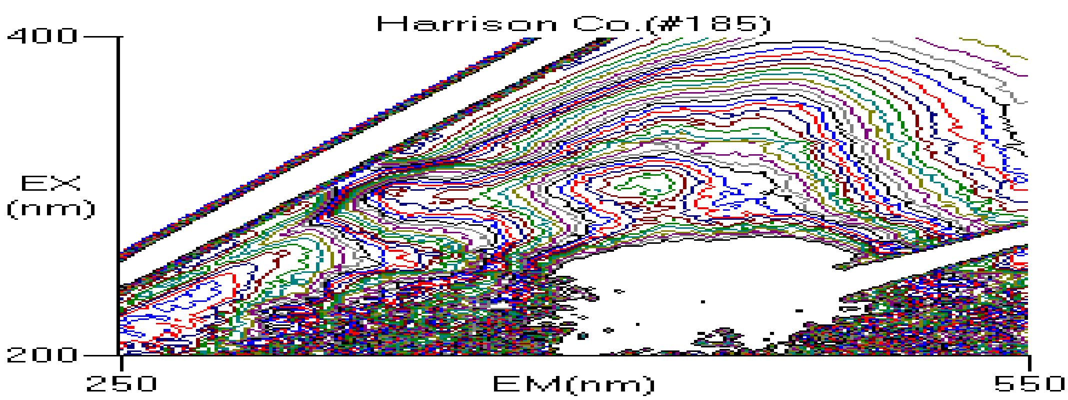

Figure 11

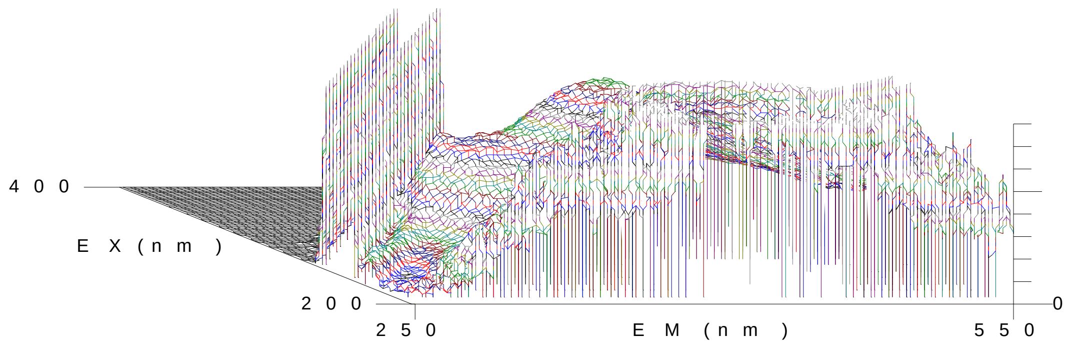

Figure 12

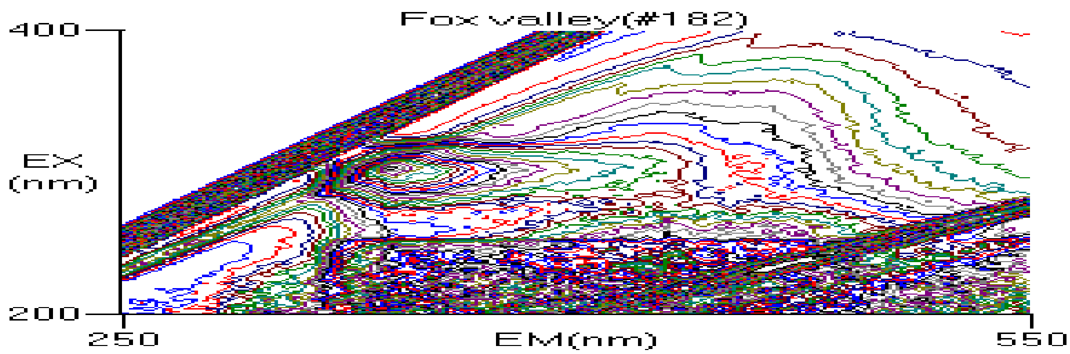

Figure 13

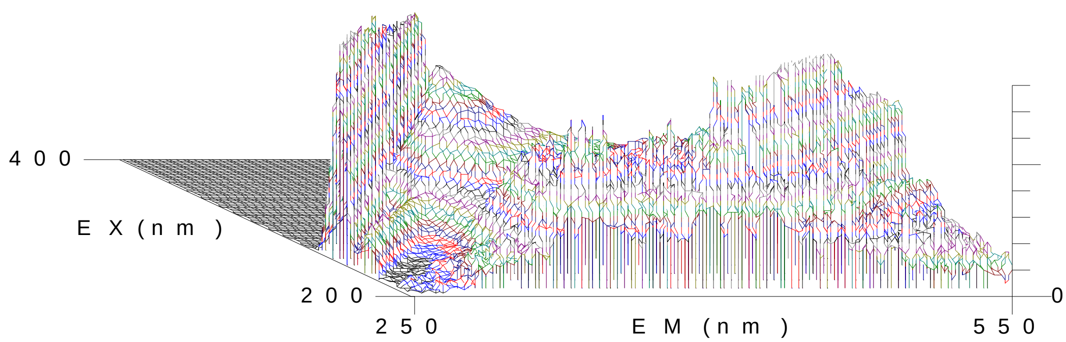

Figure 14

<u>Summary</u>

We have made significant progress in the first stage of this research, including (i) procurement, installation, and testing of the a Hitachi F-4500 fluorescence spectrophotometer; (ii) analysis of pure water samples and individual chemical dissolved in water; and (iii) analysis of 60 Missouri water samples from various lakes and water supplies. Different chemicals show substantially different characteristics of fluorescence spectra. Water samples also show different characteristics. Further research is under way to establish the relationship between the fluorescence features of individual chemicals and natural water samples, and between fluorescence features of natural water samples and water quality parameters such as NDMA formation potentials.

Literature cited

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